

SUPPORT FOR AMENDMENTS

Claims 13 and 14 have been amended for clarity. Support can be found in the claims as originally filed. Additional support for the amendment to claim 14 can be found in the specification at page 8, lines 2-4. Claims 29-32 have been newly added. Support can be found in Fig. 1.

No new matter has been added.

REMARKS/ARGUMENTS

Claims 1, 5, 8-12, 21, 29, and 31 relate to anode materials for lithium ion secondary battery comprising a coated graphite powder, which is a graphite powder in which interior portions of fine pores are coated with a carbonized material of thermoplastic resin, wherein the coated graphite powder satisfies the following five characteristics (1) through (5): (1) a mesopore volume defined by IUPAC is 0.01 cc/g or less as calculated with the BJH method as viewed from desorption isotherm; (2) an average particle size as measured by a laser-scattering- particle-size-distribution measuring device ranges from 10 μm to 50 μm , and a ratio of standard deviation to the average particle size, σ/D , is 0.02 or less; (3) a peak strength ratio R of 1,360 cm^{-1} to 1,580 cm^{-1} is 0.4 or less as determined by a Raman spectrum analysis with a wavelength of 532 nm, where $R = I_{1360}/I_{1580}$; (4) a rate of oxidation loss when oxidized in atmospheres of 400°C and an air mass flow of 3 L/min. for one hour is 2 wt% or more; and (5) a specific surface area is in the range of 1.6 m^2/g to 3.1 m^2/g as calculated based on BET with nitrogen as the absorptive.

Claims 13-20, 28, 30, and 32 relate to anode materials for lithium ion secondary battery comprising a mixture of two different coated graphite powders different in average particle size from each other, which are each graphite powders in which interior portions of fine pores are coated with a carbonized material of thermoplastic resin, wherein the mixture

of coated graphite powders satisfies the following two characteristics (1) and (2): (1) a mesopore volume defined by IUPAC is 0.01 cc/g or less as calculated with the BJH method as viewed from desorption isotherm; and (2) an average particle size as measured by a laser-scattering-particle-size-distribution measuring device ranging from 10 to 50 μm , and a ratio of standard deviation to the average particle size, σ/D , of 0.02 or less.

Claims 22-24 relate to processes for the making anode materials according to claim 1, comprising: i) dry-blending a first graphite powder with a first resin powder to form a mixture; and ii) baking said mixture in the presence of nitrogen or argon gas to obtain a baked graphite powder.

Claims 25-28 relate to process for the making anode material according to claim 13, comprising: i) dry-blending a first and second graphite powder with a first resin powder to form a mixture; and ii) baking said mixture in the presence of nitrogen or argon gas to obtain a first and second baked graphite powder.

The rejection of Claims 1, 5, 8-12, and 21 under 35 U.S.C. § 102(e) or alternatively under 35 U.S.C. § 103(a) in view of U.S. Patent 6,596,437 (*Yoon et al.*) is respectfully traversed. This cited reference discloses active materials for negative electrode used in lithium-ion battery and method of manufacturing the same. However, there is no disclosure in this cited reference of graphite powders where, upon coating with a resin, the interior pores are coated with the resin.

Yoon et al. discloses different processes of making anode materials from those disclosed in the present application. The cited reference states (with emphasis added):

During the reflux reaction, a variety of functional groups such as a hydroxy group and a hydroxyl carbon or carboxyl group, present on an edge of the crystalline carbon material, ***are condensation-reacted*** (e.g., ether combination) with a functional group present in the amorphous carbon precursor

such that a combination material of the crystalline carbon and the amorphous carbon precursor is formed.

See Col. 3: 25-33 of this cited reference. The result of this "condensation-reacted" is (with emphasis added):

[an] active material ...[that]... comprises a crystalline carbon core 1, and an amorphous carbon or a turbostratic structure carbon shell 2 *evenly covering the crystalline carbon core 1*.

See Col. 5: 18-22 of this cited reference. That is, the coating described in the cited reference is the chemical bonding of a carbon precursor to *evenly* coat a surface of the crystalline carbon. The cited reference contains no disclosure that mesopores are present in the crystalline carbon. Thus, this "evenly" covering is located to an outer surface of this core. This reference contains no disclosure that mesopore surfaces are coated.¹

In contrast, in making the presently claimed anode materials, dry graphite powder is dry blended with a dry resin powder (see Claims 21-28). Thus, the "condensation-reacted" of *Yoon et al.* does not occur in the method of making the graphite powders of the present claims. The result of this dry blending is that, for the graphite particles used in the present invention, the *interior portions* of the fine pores of the graphite particles are coated with resin. Therefore, the mesopore volumes of graphite particles in the presently claimed anode materials are reduced, which results in superior performance in irreversible capacities (28.2 to 43.6 mAh/g - see Claims 29 and 30) and initial efficiencies (90.4 to 93.4% - see claims 31 and 32) when compared to the disclosure of *Yoon et al.* (45.2 to 73.6 mAh/g and 82.8 to 89.4 – see Table 2 at Col. 9).¹

Applicants submit herewith a declaration under 37 C.F.R. § 1.132 where data is presented showing graphite particle powders made by the presently claimed processes and graphite particle powders made by the processes of *Yoon et al.* Table 1 of the declaration is reproduced below:

¹ For illustrations of the coatings of the presently claimed graphite powders and the coatings of the *Yoon et al.* powders, please see pages 8-11 of the response filed October 27, 2008.

Table 1: Average interlayer spacing d(002) of anode material before and after resin coating.

Added amount of PVA (parts by weight with respect to 100 parts by weight of natural graphite)	d(002) (nm)
0 (no coating)	0.3554
10	0.3354
50	0.3355
100	0.3354

*Although 50 parts by weight of PVA is adopted in the examples of the present application, it is understood that d(002) does not change even in the case of 100 parts by weight.

As the Examiner will note, the average interlayer spacing, d(002), of the graphite particle powders made by the presently claimed processes exhibit only minor differences as more resin is applied to the powders (see Table 1 of the declaration). In contrast, the average interlayer spacing of graphite powders made by the processes disclosed in *Yoon et al.* increases once the resin is applied (d(002) = 3.35 Å prior to coating; d(002) = 3.41 Å after coating). This effect in interlayer spacing signifies that the mesopores of the presently claimed powders are coated during the presently claimed processes, while the coating in *Yoon et al.* is limited to the exterior portions of the graphite powders. The fine pores of the *Yoon et al.* graphite powders are not coated by the methods disclosed therein.

In view of the above, Applicants have demonstrated that the average interlayer spacing of the presently claimed graphite powders made by the presently claimed processes does not change when resin is applied to the graphite particles, while graphite particle powders made by the processes disclosed in *Yoon et al.* **do** exhibit an increased average interlayer spacing. As a result, the mesopores of the presently claimed graphite powders are coated with resin, while any fine pores of the *Yoon et al.* graphite powders are **not** coated with resin. *Yoon et al.* contains no disclosure of dry-blending graphite powders with resins. Therefore, the coating of the mesopores and properties achieved thereby (e.g., mesopore volume) are **not** inherent to the processes disclosed in *Yoon et al.*, and Applicants maintain that one of ordinary skill in the art would not expect to achieve the Applicant's superior results from the disclosure of *Yoon et al.*.

Accordingly, the rejection should be withdrawn.

The rejection of Claims 13-20 and 28 under 35 U.S.C. § 103(a) in view of *Yoon et al.* and Japanese Patent Publication 2001-196097 (*Aihara et al.*) is respectfully traversed. Like *Yoon et al.*, *Aihara et al.* contains no disclosure of dry blending graphite powders with resins (a machine translation of *Aihara et al.* is submitted herewith). Furthermore, *Aihara et al.* does not disclose the mixing of a first graphite powder with a second graphite powder that has an average particle size, prior to coating with a thermoplastic resin, ranging from 10–13 µm (see Claim 14). Thus, for the same reasons given above, the combined disclosures of these cited references would not suggest to one of ordinary skill in the art the presently claimed graphite powders nor methods of making the presently claimed graphite powders.

Accordingly, the rejection should be withdrawn.

The rejection of Claim 13 under 35 U.S.C. § 112, 2nd ¶, has been obviated by appropriate amendment to the claims. Accordingly, the rejection should be withdrawn.

Applicants submit that the present application is in condition for allowance.

Notification thereof is earnestly solicited.

Respectfully submitted,

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

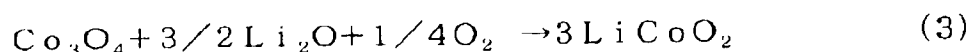
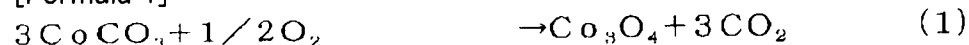
[Field of the Invention]This invention relates to a lithium secondary battery.

[0002]

[Description of the Prior Art]The constituent which uses suitable LiCoO_2 to be conventionally used as a positive electrode material for lithium secondary batteries, or LiCoO_2 as the main ingredients, LiCoO_2 using such a positive electrode material mixed a cobalt compound and lithium salt with the suitable mixture ratio, and was calcinated and compounded by relatively high temperature. For example, according to literature (Mizushima et al. [Mat.Res.Bull.15(1980)783 K]). after carrying out preliminary calcination of CoCO_3 and the Li_2CO_3 in the air for 900 ** and 20 hours, calcination (detailed temperature conditions -- unknown) of two times was performed, and suitable LiCoO_2 was compounded. The pyrolysis of CoCO_3 and Li_2CO_3 which were mixed is carried out at an elevated temperature, they react while they emit CO_2 gas, and they generate LiCoO_2 .If this reaction is guessed, it will be thought that it is expressed with the reaction formula probably shown below.

[0003]

[Formula 1]



[0004]It is the feature that (1) and (3) need excessive oxygen with this reaction formula. If Co_3O_4 is used as a starting material from the beginning instead of CoCO_3 , the consideration to the reaction of (1) type will become unnecessary. Therefore, it is thought [rather than] using CoCO_3 that there is a place where it is more convenient practically to use Co_3O_4 . Composition using the peroxide of lithium may be performed depending on the case (for example, shown in literature (M. G.S.R.thomas et al Mat.Res.Bull., 20(1985)1137)).

[0005]Thus, although many know how exists and patent application is carried out involving the optimal synthesis method etc., this constituent has a fundamentally high electric resistance value, and, according to literature (J, Phys, Chem, Solids, 48, 97 (1987)), they are 100 ohm-cm. When an electric resistance value creates an anode using a high positive electrode material intrinsically, electronic conduction ohm loss cannot avoid the disadvantage which becomes large. As for LiCoO_2 , hypoxia exists. If an oxygen deficiency increases, maintenance of the layer structure will become

difficult.

[0006]On the other hand, in a lithium secondary battery, although the lithium metal simple substance was used as a negative pole material before, there were problems -- an arborescence deposit of a lithium metal causes an internal short circuit. Therefore, in recent years, carbon is used as a negative pole material and the method of inserting a lithium ion and desorbing it is becoming in use. By using this electrode, it has voltage comparable as the case where a lithium metal is used, and the cell with high safety which moreover does not have an arborescence deposit became possible. The composition of this negative electrode is made to bind using a binder using carbon materials, such as pyrolytic carbon, carbon black, corks, and graphite, for shaping.

[0007]The binder is added and pasted up in order to use positive active material like LiCoO_2 as a component of an anode as the main ingredients, to add black lead etc. in order to raise conductivity, and to give moldability like a negative electrode.

[0008]After these electrodes is mainly carried out [film shaping] by a wet compaction method, in order that the charge-and-discharge capacity per unit volume may be raised, the method to which an active material filling factor is made to increase is taken by carrying out press compression.

[0009]In the conventional lithium secondary battery, a separator is made to intervene between the above-mentioned two electrodes, the nonaqueous organic solvent is used as an electrolysis solution, and battery structure has a coin type or a cylindrical square shape. When making a high current profitably like in a cell generally, to enlarge an electrode area as much as possible is tried. Especially in a lithium secondary battery, since the comparatively low organic solvent of conductivity is used as an electrolysis solution, large area-ization of an electrode becomes important especially.

[0010]Drawing 38 is the conventional coin type cell shown in 124 pages of a "cell manual" (the volume on cell manual member-of-editorial-board meeting, Maruzen Heisei 2 issue). As for a positive active material layer and 2, in a figure, a separator and 10 are sealants a negative electrode active material layer and 3 1. With the flat cell of such a structure, there is a limitation in enlarging an electrode area and the cylindrical cell which enlarged the electrode area is made from winding up a band-like electrode as a cell of the type which takes the fact and a high current. In order to obtain a large area using a plate-like electrode, the conventional method took the structure which connects the so-called strip-of-paper-like electrode.

[0011]Drawing 39 is the structure of the conventional clad type lead battery similarly shown in 188 pages of a "cell manual" (the volume on cell manual member-of-editorial-board meeting, Maruzen Heisei 2 issue). Both the strip-of-paper-like anodes 1 and negative electrodes 2 are tied by a collecting tab and the connecting rod like a ctenidium, are arranged via the separator 3, and are put in by one container.

[0012]As a method of obtaining a large area electrode, folding battery structure which is indicated to JP,4-298973,A is advocated. Face the active material and the anode board which applied positive active material to one field of the current collection substrate which consists of a band-like metallic foil is used as 2 chip boxes, Between the right polar plate which carried out 2 chip boxes, a negative electrode plate is inserted via a separator, a band-like group of electrode is formed, and it is considered as square-shaped electrode structure by bending the group of electrode by turns, and folding it by fixed width.

[0013]As an important index in development of a lithium secondary battery, two, service capacity and a cycle life, are mentioned. In the service capacity of a rechargeable battery, there are two kinds of how, the service capacity per active material weight and the service capacity per unit volume, to express. A cell excellent in both this performance is desired. The size changes by the ability of the carbon whose service capacity per weight is an electrode active material, or an inorganic oxide to permit insertion and secession in the reaction of a lithium ion only in which. It is influenced by whether the presentation of each electrode and structure are in the state where lithium reacts easily. It is dependent on the quantity of the electrode active material filled up with

the service capacity per unit volume into unit volume on the other hand. That is, the filling factor of an electrode active material is greatly concerned with the service capacity per unit volume. Since this filling factor was influenced by the particle diameter of an active material, and the presentation of the electrode, it was possible to raise the service capacity per volume by [these] inquiring, but this examination was seldom performed conventionally.

[0014]Another of the improvement in a cycle life is mentioned as the characteristic of a lithium secondary battery. As shown previously, the lithium metal was used for the negative electrode of the lithium secondary battery before, but the cycle life has improved substantially by using carbon. However, since the fall of the capacity by charge and discharge is produced also in carbon, improvement of carbon material is needed. For this reason, the negative electrode was conventionally created using the carbon created by various raw materials and manufacturing conditions.

[0015]

[Problem(s) to be Solved by the Invention]About the generation and decomposition of LiCoO_2 at the time of composition of LiCoO_2 , it seldom searched from the former as mentioned above. That is, there were no reply and report to the problem to what times a temperature-up maximum is permissible, as calcination temperature conditions. There was no detailed report also about the technique of how the Li/Co ratio of LiCoO_2 or its stoichiometry (O/Co ratio) is controlled thru/or adjusted. That is, the evaluation methods thru/or the technique of evaluation were not fully established about the point what kind of feature LiCoO_2 with is the most outstanding constituent as a positive electrode material for lithium secondary batteries.

[0016]Therefore, LiCoO_2 of what kind of firing condition is making the actual condition description of what kind of the rechargeable battery characteristic is shown from beginning to end. Of course, searching for the firing condition that a powder X diffraction is performed, for example, the ratio of the peak (it will be near $2\theta = 18.8$ degrees if $\text{CuK}\alpha$ rays are used) from the field where intensity is the largest (003) to the peak (near $2\theta = 45.2$ degrees) whose intensity is [second] the largest becomes large is performed. However, such a technique was required as evaluation methods of LiCoO_2 so that artificers might clarify, but it was not enough.

[0017]Although artificers found out that a quite big exoergic reaction (about 40 cal/g) followed on composition of LiCoO_2 , if a part for this generation of heat is not diffused well enough, fired material will cause unexpected temperature up. It was impossible in powder X-ray diffractometry to have detected the history of such unexpected temperature up which is not preferred.

[0018]On the other hand, examination is advanced also about the possibility of low-temperature composition from high temperature firing being next to the pyrolysis which is not preferred for LiCoO_2 , and there being many hypoxia yields. For example, according to literature (Mat.Res.Bull., 27 (1992) 327 Gummow), low-temperature 400 °C composition for one week is tried using CoCO_3 and Li_2CO_3 . However, since a remarkable elevated temperature is needed for the pyrolysis of carbonate, it must be said that such a trial has unreasonableness. Since LiOH will always absorb CO_2 out of the air and Li_2CO_3 will be generated although there is possibility of low-temperature composition if it changes to Li_2CO_3 and LiOH is used, The amount of mixture of Li_2CO_3 had to be monitored continuously, therefore difficulty followed on holding and controlling the Li/Co ratio in fired material uniformly.

[0019]It may be eventually impossible for to give many desirable features only by a firing process. Although a possibility of giving many desired features is hardly examined by post-processing, if it becomes realizable, in composition of LiCoO_2 , it cannot suspect becoming practical big progress.

[0020]In order to make high the low electrical conductivity of a positive electrode material, usually

adding about 10% of graphite powder to LiCoO_2 , and creating an anode has been performed. Addition of such a conducting material also had the problem of causing the capacity lowering of a cell in order to reduce the ratio of an original positive electrode material.

[0021]The lithium secondary battery which has the folding structure advocated until now, For example, in order to have structure as shown in above-mentioned JP,4-298973,A and to realize this structure, the electrode and the separator were bent with very small curvature, and the member had to be very flexible in order to realize this processability. It is a porous body of the polymer which has a thickness of about 25 micrometers, and a separator is comparatively rich in pliability and its intensity is also high. However, a positive electrode layer and a negative electrode layer make a granular material bind with a little binding materials, and are comparatively inferior in pliability, and their intensity is also low. For example, when the electrode plate fabricated on current collecting foil was folded up, when it became smaller than a value with bending curvature, the crack arose in the electrode active material layer, and there was also a problem of it becoming impossible it to not only to become a manufacture top problem, but to fully pull out electrode capability at the time of battery operation.

[0022]In order that large scale-ization may be desired and the present lithium secondary battery may raise the capacity per cell, thickness of an active material layer is made thicker, or examination which compresses an active material layer with a press etc. and raises an active material filling factor is advanced. It is inferior to pliability and the assembly of a fold-up cell which does not make an active material layer produce a crack becomes still more difficult, so that an active material layer becomes thick, and, so that an active material filling factor becomes high.

[0023]Even if it was able to perform the assembly of the fold-up cell that there is no crack in an electrode active material layer, when it uses carbon for negative electrode active material and cobalt acid lithium etc. are used for positive active material, both will swell at the time of charge and tensile stress will arise in the current collecting foil to which it was stuck by the electrode layer. Since this stress will become larger in a bending portion in the case of a fold-up structure, when charge and discharge were repeated, current collecting foil etc. may have been torn, and it may have become impossible collecting a current.

[0024]In addition, if contact of each member is not good when an anode and a negative electrode counter, are piled up via a separator and a cell is formed, electrode performance cannot fully be pulled out. Cell area becomes large, and the problem of contact will become still more serious if member lamination number of sheets increases by a fold-up structure etc.

[0025]There is an increase in service capacity as one of the technical problems of development of a lithium secondary battery. As described above, about the service capacity per volume, improvement in the filling factor of an active material serves as a technical problem. Although what has single mean particle diameter was conventionally used as an electrode active material, there is a limit that mean particle diameter is single in the rate of the closest packing of that active material (drawing 40), and the filling factor of that granular material decreases, so that this mean particle diameter becomes small (drawing 41). That is, when a granular material volume fraction (PVC) increases from drawing 40, it turns out that the granular material filling factor ϕ goes up, but it turns out that the filling factor of a granular material becomes fixed from a certain point (CPVC).

[0026]The conducting agent and the forming assistant are contained in the anode as a presentation with the active material, and the active material and the forming assistant are contained in the negative electrode. In this case, the filling factor of an active material changes with ratios of the active material under presentation. However, in the closest packing in the composition ratio performed now, the service capacity per volume was not a value satisfied not necessarily. In order that the binder which is a forming assistant might bind granular materials, such as an active material, it had added, but when there were too many these binder amounts, the thickness which covers the surface of a granular material became thick, and it became a problem to have checked the reaction of an active material.

[0027]One of the problems of development of a lithium secondary battery has the fall of a cycle life. The long carbon of the cycle life is examined by creating a negative electrode using various kinds of carbon material especially in a negative electrode. However, the problem that the deduction coefficient of capacity in charge and discharge was large produced the carbon with large service capacity. With the carbon with large capacity as this cause, it was thought that there was a deposit of the lithium metal in the fall of the potential of an electrode. Since reactivity was lost by metal-ization of this lithium ion, the short circuit inside the capacity lowering by the shortage of a lithium ion or a cell arose, and the cycle life was falling.

[0028]This invention was made in order to cancel the problem of the above lithium secondary batteries, and it presents the lithium secondary battery which was excellent in service capacity and a discharge cycle characteristic.

[0029]

[Means for Solving the Problem]In a lithium secondary battery using [a lithium secondary battery of this invention / using an inorganic oxide as positive active material] carbon as negative electrode active material, When mean particle diameter of an inorganic oxide which is positive active material, or carbon which is negative electrode active material comprises at least two or more sorts and sets a large drop child's particle diameter to 1, a ratio of a granule child's particle diameter is 0.3. It is the following.

[0030]Lithium secondary batteries of this invention are at least two or more kinds of things with which carbon which is negative electrode active material differs among a raw material, manufacturing conditions, or the characteristic in a lithium secondary battery with which negative electrode active material comprises carbon, and are constituted.

[0031]In a lithium secondary battery with which a lithium secondary battery of this invention comprises an inorganic oxide whose anode presentation is positive active material, black lead which is conducting agents, and a binder which is forming assistants, When a binder is covered by the surface of positive active material which is a granular material, and a conducting agent, a range of average covering thickness t_B (nm) of a binder is $3 \leq t_B \leq 16$.

[0032]In a lithium secondary battery with which a lithium secondary battery of this invention comprises an inorganic oxide whose anode presentation is positive active material, black lead which is conducting agents, and a binder which is forming assistants, When an active material makes x_{AC} an active material volume fraction used as the closest packing, graphite body integration rate x_G is in the range of $(1-x_{AC}) / 3 \leq x_G \leq 1-x_{AC}$.

[0033]A lithium secondary battery of this invention has the voidage P (%) in an electrode in the range of $10 \leq P \leq 30$ in a lithium secondary battery which uses carbon as negative electrode active material using an inorganic oxide as positive active material.

[0034]

[Embodiment of the Invention]The reference example 1. reference example 1 is explained.

Commercial Co_3O_4 powder was put into 1 kg and an alumina crucible, and it put in the electric furnace which set temperature as 925 **, and calcinated in the air for 3 hours. Although the cobalt oxide always contains basic undecomposed cobalt carbonate (2CoCO_3 and $3\text{Co}(\text{OH})_3$), it is 900–950 **, and by calcinating in the air, it decomposes and a presentation is unified into Co_3O_4 .

Respectively, the X diffraction result of the back before heat treatment (inside of 925 ** 1 hour and the air) of a cobalt oxide is shown, O seal shows LiCoO_2 and, as for drawing 1 (a) and (b), x seal shows basic cobalt carbonate. It turns out that basic cobalt carbonate disappears thoroughly and serves as a pure Co_3O_4 presentation by this heat treatment from a figure.

[0035]332.52g of Li_2CO_3 was taken to this calcination powder 722.4g, and it often enough mixed and ground in the dry type ball mill to it for 5 hours. Next, press forming of the powder mixture is carried

out to a Plastic solid (50 mm in diameter, and 5 mm in thickness) by press pressure 500 kg/cm^2 , The fragment of the 1-mm-thick alumina spacer was put between the suitable place of a press-forming object several places, and temperature up was carried out from the room temperature to 740°C with the heating rate of 5°C/min for 1 minute, and it was calcinated at 740°C among the air for 10 hours. The back held for 20 hours, after carrying out temperature up to 820°C with the heating rate of 5°C/min for 1 minute succeedingly as it was. The back turned off the electric furnace and it cooled to the room temperature as it is. After grinding the taken-out calcination powder for 2 hours using a dry type ball mill, the big particles more than 20 micron m were removed with the mechanical sieve.

[0036]Generation of heat of the LiCoO_2 synthetic reaction was made easy to radiate by establishing a crevice suitable between Plastic solids, while becoming easy to follow a LiCoO_2 synthetic reaction by carrying out press forming and fabricating a press-forming object thinly. By performing two-step calcination, generation of heat at the time of LiCoO_2 composition was made to further fully radiate, the rise in heat at the time of calcination was pressed down at 900°C or less, and the unexpected rise in heat was prevented effectively.

[0037]That is, artificers acquired the following knowledge about the generation and decomposition at the time of LiCoO_2 composition wholeheartedly using thermometric analysis as a result of the pursuit. The measurement result of TG-DTA showing decomposition of LiCoO_2 is shown in drawing 2. A solid line is DTA and a dotted line is change of TG. It decomposes at 1130°C and the LiCoO_2 itself generates Co_3O_4 again (X diffraction data is omitted). Heat of decomposition is about 82 cal/g . Therefore, it is obvious that the synthesizing temperature of LiCoO_2 must not exceed this

temperature. Moreover and also artificers checked that an ambiguous decomposition temperature region existed in $930\text{--}1030^\circ\text{C}$ from the X diffraction result of the sample which changed calcination temperature, as shown in drawing 3. This decomposition temperature region is checked also from the infrared absorption spectrum shown in drawing 4. As for the infrared absorption spectrum of a heat treatment sample, and a horizontal axis, wavelength (micron) and the vertical axis of drawing 4 (a) are transmissivity. A number shows a peak wave number (cm^{-1}). (b) is an extinction quotient (absorption band [of 247 cm^{-1}]/– absorption band of $600\text{--}\text{cm}^{-1}$) of a sample same as the above. A horizontal axis shows a wave number (cm^{-1}), and a vertical axis shows an extinction quotient. It is also clearer in composition of LiCoO_2 that temperature up must not be carried out across this decomposition temperature region ($930^\circ\text{C} - 1030^\circ\text{C}$) than in this. If temperature up is carried out to 1000°C , he can understand the fact of deteriorating in a heterogeneous thing, from drawing 4.

[0038]However, in order not to carry out temperature up of the sample to not less than 900°C at the time of composition of LiCoO_2 , it is not enough just to hold the preset temperature of a furnace at 900°C . The problem of the calorific value of the synthetic reaction described next artificers found out exists.

[0039]drawing 5 -- the result of thermometric analysis (TG-DTA) -- quantity of heat was shown in Table 1.

[0040]

[Table 1]

Li/Co比	吸熱 (cal/g)		発熱 (cal/g)	吸熱 (cal/g)	
		減量分基準*			減量分基準
0.6	13.4	129.4	1.2	74.2	2655
0.8	29.5	220	20.9	40	3060
1.0	48.4	340	38.5		
1.2	49.0	356	36.5		

[0041]The Li/Co ratio of a sample is four sorts of 0.6, 0.8, and 1.0 and 1.2. Co_3O_4 and Li_2CO_3 were used for this experiment. Speaking of the constituent of Li/Co=1, after an endothermic peak (amount of endothermics 48.4 cal/g) begins from 675 **, it ends at 735 **. Then, an exoergic reaction starts promptly and it ends before 900 **. This calorific value ΔH is 38.5 cal/g. Since the specific heat of a sample is abbreviation 0.2 cal/g**, the calorific value at the time of LiCoO_2 composition will be a size which is sufficient for carrying out temperature up of the sample about 200 degrees, if it thinks that it generates in the state of heat insulation. That is, if a part for this generation of heat is not made to emit well enough, it can guess that sample temperature exceeds 900 ** easily. In fact, when a sample was calcinated in large quantities, even if it was keeping the temperature of the furnace at 900 **, it was not able to avoid carrying out temperature up exceeding 900 **.

[0042]Generation of heat was made to fully emit, and in order to prevent the unexpected rise in heat over 900 **, two-step calcination was performed. As the first step of calcination temperature region, 735–785 ** is preferred. Thereby, most portion of the calorific value from 735 ** can be made to emit by the low temperature side. Then, temperature up is carried out from 785 ** to 850 **, and the second step of calcination is performed. At this time, since a great portion of generation of heat of the synthetic reaction of LiCoO_2 is made to have radiated previously, it is hard to produce an unexpected rise in heat. This purpose can be certainly attained by inserting the thermo couple for coke-oven-temperature control in a core in the midst of calcination powder.

[0043]In order to advance the synthetic reaction of LiCoO_2 , powder is fabricated by the pressure of 100 kg/cm^2 to 1000 kg/cm^2 . What is necessary is for a suitable pressure range to take into consideration the size of the metallic mold to be used, the performance of a stock pressing machine, etc., and just to decide it. In order for the thickness of a Plastic solid to make generation of heat of a LiCoO_2 synthetic reaction radiate quickly enough at this time, 2–10 mm is preferred. It is difficult for the inside of a Plastic solid to be filled with reaction fever easily, if it is not less than 10 mm, and to pick out a Plastic solid from a golden form in 2 mm or less.

[0044]Emission of reaction fever and improvement in a filling factor can be aimed at by keeping a 1–2-mm gap and laminating a Plastic solid at the time of calcination. Although the X diffraction intensity of a powder sample and a press sample was shown in Table 2, by pressing shows becoming easy to follow a synthetic reaction.

[0045]Evaluation of calcinated LiCoO_2 can be roughly performed by powder X-ray diffractometry, as stated previously. For example, it was shown in Table 2, [0046]

[Table 2]

回折線	粉末 (CPS)	プレス試料 (CPS)
45°	390	764(1.96 倍)*
37°	125	261(2.09 倍)
18°	337	479(1.42 倍)
18° /45°	.86	.63(.73 倍)
18° /37°	2.70	1.84(.68 倍)

* : 粉末のものとの比

[0047]It is seeing the absolute intensity of three powerful diffraction lines (45.2, 37.3–18.8 degrees), or seeing those ratios 18.8/45.2 and 18.8/37.3. However, as explained previously, the knowledge of an X diffraction does not give detailed information.

[0048]Next, the appraisal method by infrared absorption is described in detail. The portion of the Co–O elastic absorption band which lengthened the baseline was shown in drawing 6. The slash field which it has focusing on about 600 cm^{-1} is Co–O₆ (in LiCoO₂, Co is enclosed by six oxygen and). Li is also enclosed by six oxygen and it is thought that the remaining tail parts are based on Co–O_{6-x} (portion from which a part of oxygen escaped). When the former was called the normal portion (A), the latter was called the un-normal portion (B) and reciprocal ratio B/A (an un-normal portion / normal portion) of both area was taken, it became clear that this ratio relates to the stoichiometry (O/Co) of LiCoO₂ (drawing 7). Area is measured with a planimeter etc. Therefore, the stoichiometry can be easily evaluated by mixing several mg sample powder to 0.3–g iodine caesium powder, creating a briquette sample, and measuring with infrared spectrograph.

[0049]The infrared absorption spectrum at the time of replacing Li7 which is an isotope of lithium in LiCoO₂ by Li6 was shown in drawing 8. By Li6 substitution, since it is clear to shift the absorption band of 279 cm^{-1} to 292 cm^{-1} , and to shift the absorption band of 229 cm^{-1} to 239 cm^{-1} , it can be concluded that these two absorption bands are the things based on Li–O vibration. As compared with the theoretical value (7/6 of square roots) 1.08 of a shift ratio, both shift ratios of both are slightly as small as 1.04. It is thought that 247 cm^{-1} of two absorption band and 224 cm^{-1} which are not shifted are what is depended on O–Co–O deformation vibration. It was shown previously that the extinction quotient of a 247 cm^{-1} absorption band and a 598 cm^{-1} absorption band changes to drawing 4 reflecting a firing condition a lot than X diffraction intensity. Therefore, it can be considered that this extinction quotient is the completeness of Co–O₆ combination. It is because O–Co–O deformation vibration reflects the completeness of an omnidirection crystal structure.

[0050]The stoichiometry (O/Co) of LiCoO₂ and the completeness of Co–O₆ combination were able to be evaluated from the infrared absorption spectrum of $1000\text{--}200\text{ cm}^{-1}$ so that clearly from having stated above. The completeness of Co–O₆ combination is a leading index of the completeness of the layer structure of a LiCoO₂ crystal, and artificers are checking that the one where this is higher enough has the characteristic outstanding as a positive electrode material. It is obvious that the direction of the good constituent of stoichiometry has the characteristic outstanding about the receipts-and-payments capability of lithium. Therefore, since these two parameters reflect the positive electrode material characteristic of LiCoO₂ greatly, they can be made into the standard which judges the quality of the constituent which uses LiCoO₂ suitable as a positive electrode material for lithium secondary batteries, or LiCoO₂ as the main ingredients. As mentioned above, it became clear from an infrared absorption spectrum that two important parameters of LiCoO₂ can

be evaluated.

[0051] After taking 1–2 mg of powder created by the above-mentioned reference example 1 and mixing with 0.3-g iodine caesium powder well, With a press, fabricate to a tablet 13 mm in diameter (compacting pressure is $2\text{--}t\text{ [}/\text{cm}^2\text{]}$), and with the infrared spectrograph 883 by PerkinElmer, Inc.

When the infrared absorption spectrum between 200 cm^{-1} [from 1000 cm^{-1}]⁻¹ is measured, as an index of an O/Co ratio, As for the extinction quotient of 0.7 and $247\text{ cm}^{-1}/600\text{ cm}^{-1}$, 1.5 was obtained when asked for the surface ratio of (the un-normal part / normal part).

[0052] It may be pressed for reference example 2. calcination powder by the necessity that do not always have a desired parameter and suitable post-processing adjusts also including X diffraction intensity. In such a case, it is changeable to desired parameter value by choosing 500–900 ** for heat treatment temperature, choosing the suitable value between pure oxygen for oxygen tension from air, and heat-treating according to the value of two parameters of the sample. This is for LiCoO_2 powder to adjust the amount of oxygen according to the post-processing condition during post-processing, and for a crystal structure to become perfect more. The example of three samples (A, B, C) was shown in Table 3.

[0053]

[Table 3]

試料 ピーク	A		B		C
	空気	O ₂	空気	O ₂	空気
45.2°	0.63	0.76	0.88	1.09	1.00
37.3°	0.72	0.73	1.09	1.02	1.01
18.8°	0.80	1.42	0.88	0.99	1.52

[0054] The sample A can raise the intensity of a peak 18.8 degrees by calcination among O₂. The sample B is calcination among the air and can raise the intensity of a peak 45.2 degrees in a 37.3-degree peak and O₂. The sample C can raise the intensity of a peak also by calcination among the air 18.8 degrees.

[0055] The iodine caesium tablet of the LiCoO_2 powder of reference example 3. marketing was made, and the infrared absorption spectrum between 1000--cm^{-1} – 200--cm^{-1} was measured. As a result, B/A surface ratio was 0.7 and the completeness of Co–O₆ combination was 0.64. In 900 ** and the air, this powder was calcinated for 2 hours and furnace cooling was carried out. The iodine caesium tablet was made after heat treatment, when the infrared absorption spectrum was measured and evaluated similarly, B/A surface ratio increased to 1.15, but the completeness of Co–O₆ combination was not different from 0.69. When the anode was created, the lithium cell was manufactured using the powder after this heat treatment and the charging and discharging characteristic was measured, compared with the powder before heat treatment, the characteristic has been improved substantially.

[0056] To reference example 4. Co_3O_4 240.8g (1 mol), weighing of Li_2CO_3 88.67g (1.2 mol) and LiHCO_3 40.76g (0.6 mol) was carried out, and it mixed well with the ball mill. In the reference example 1, after carrying out press molding of the powder to calcinate, the case where two steps were calcinated was described, but after not carrying out press molding of the powder but inserting the thermo couple for coke-oven-temperature control in a core in the midst of powder with powdered voice, it calcinated in the 25-hour air at 900 **. Since generation of heat by a synthetic reaction accumulates inside calcination powder and the input to an electric furnace is finely controllable according to a part for the temperature up inside powder if the thermo couple for coke-

oven-temperature control is inserted in the core in the midst of calcination powder, there is no fear of a rise in heat breaking out exceeding 900 **. Since there is a tendency for a core to become an elevated temperature most in the midst of powder, that the midst inserts a thermo couple in a core can always detect the maximum temperature of calcination powder. When evaluated with infrared spectrograph, the completeness of LiCoO_2 and Co_3O_4 combination of the B/A ratio was 2.0.

[0057]When [which is reference example 5.] compounding LiCoO_2 in the above-mentioned reference example 1, compounded by mixing Li_2CO_3 to Co_3O_4 , but. It is good to compound by using the mixed lithium salt of Li_2CO_3 and LiHCO_3 for Co_3O_4 . That is, management of a Li/Co ratio is easy for LiHCO_3 , without being easier to decompose at low temperature than Li_2CO_3 , and absorbing CO_2 in the air unlike LiOH .

[0058]Reference example 6., next the reference example 6 are explained. To Co_3O_4 and 8.023 g, Li_2CO_3 was mixed by 3.283 g and NaHCO_3 and 2.511 g was mixed with the automatic mortar for 2 hours (Na addition % of 10 mol). This powder mixture was calcinated at 850 ** among the air with the electric furnace for 20 hours. It was set to 20Kohm when the electric resistance value was measured. It turns out that about 1/ of this value is set to 50 to the value of 1 M omega when not adding Na, and it becomes a conductive high active material.

[0059]The sample which replaced Na is explained further. The additions of Na were 10 and 20 or 30-mol%, it is Co_3O_4 , Li_2CO_3 , and Na_2CO_3 that were used here, and it fully ground them with the mortar. The TG-DTA measurement result about the heat action and Na addition at the time of Na addition LiCoO_2 composition is shown in drawing 9. A horizontal axis shows temperature (**) and a vertical axis shows quantity of heat. A sample is four sorts whose addition concentration is 10 and 20 or 30-mol %. TG-DTA measurement result heating-rate 10 K/min was shown. Irrespective of Na addition, near [near 350 ** to] 460 ** shows one broadcloth endothermic peak. Since there is no thermal change in addition to this, it can be surmised that Na fully replaces by Li. Change of the X diffraction intensity of this sample was shown in drawing 10. Each of three peaks with strong intensity shows straight-line relations to the addition of Na. Drawing 11 (a), (b), and (c) shows the X diffraction result at the time of scanning between angle-of-diffraction $2\theta=70 - 10$ in the addition 10 of Na, and 20 or 30-mol% respectively. What a diffraction pattern is it of LiCoO_2 fundamentally and attached v seal by the small diffraction peak NaCo_2O_2 (ASTM27-682), It seems that it is in agreement with alpha-Na 0.75CoO_2 (ASTM32-1068), beta-Na 0.6CoO_2 (ASTM30-1181), etc.

[0060]Na addition to LiCoO_2 is reported by literature (J. Power Sources, 39 (1992) 313 Bludska et al.), According to this, the sample is created using each carbonate by 400 **30hr, 650 **8hr, and 900 **8hr calcination to Na20mol%. The mobility of Li went up by Na addition, and it is concluded that Na-concentration % of 5 mol is best. According to our experimental result, Na addition exceeded 5-mol% and it was acquired that less than 30mol% is the optimal. That is, if Na addition exceeds 30-mol% and Li decreases more, the capacity of a cell will fall. If it is less than 5mol%, the mobility of Li will decrease and resistance will fall.

[0061]The sample which replaced reference example 7., next K is explained. The additions of K are 10 and 20 or 30-mol%, and what were used is Co_3O_4 , Li_2CO_3 , and K_2CO_3 . Explanation of K addition % of 20 mol mixed 3.283 g, KHCO_3 , and 2.002 g for Li_2CO_3 with the automatic mortar to Co_3O_4 and 8.023 g for 2 hours. This powder was calcinated at 850 ** among the air with the electric furnace for 20 hours. It was 43ohms when electrical resistance was measured. The measurement result of TG-DTA of this sample was shown in drawing 12. Although the endothermic peak near 360-500 ** is in the tendency which becomes so small that the addition of K increases, the endothermic peak near 850 ** (data accrued) is in a reverse tendency. The small endothermic peak near 850 ** is

seen when the applied addition does not replace by Li quickly, and also when Ag_2O and Cu_2O are added (it is for being temporarily set to $\text{Li}/\text{Co} < 1$ and producing the shortage of Li.), it is seen. The relation between K concentration and the diffraction intensity of three diffraction peaks was shown in drawing 13. It differs from the case where it is Na addition that only a peak is refracted 18.8 degrees. The diffraction peak for $2\theta = 70$ to 10 degrees was shown in drawing 14. the small peak which attached x -- attribution -- although it is unknown, a strong peak is a thing of LiCoO_2 structure.

[0062]As mentioned above, as a result of sodium and potassium replacing some lithium, in the reference examples 6 and 7 as a calcination constituent, $\text{Li}_{1-x}\text{Na}_x\text{CoO}_2$ and $\text{Li}_{1-x}\text{K}_x\text{CoO}_2$, Or $\text{Li}_{1-x}\text{Na}_{x1}\text{K}_{x2}$ ($x1+x2=x$) etc. are obtained, K ion or Na ion is incorporated in the structure of LiCoO_2 , and it becomes a conductive high active material.

[0063]Reference example 8., next the reference example 8 are explained. Since pyrolysis temperature becomes low by using as the mixed salt or the eutectic crystal hydrogencarbonate of carbonate, a hydrogencarbonate or carbonate, and a hydrogencarbonate and the low temperature baking of sodium salt or potassium salt becomes possible, little calcination powder of disorder is obtained in crystal structure. Such an example is shown. Li_2CO_3 to Co_3O_4 and 8.023 g 3.283 g, NaHCO_3 , 0.837 g, KHCO_3 , and 0.501 g were mixed with the automatic mortar for 2 hours (Na addition % of 10 mol, and K addition % of 10 mol), and this powder was calcinated at 850 ** among the air with the electric furnace for 20 hours. It was 100ohms when the electrical resistance of fired material was measured. Such NaHCO_3 , Na_2CO_3 , KHCO_3 , and K_2CO_3 to lithium salt independent, mixing and adding not only in the fall of the large pyrolysis temperature of lithium mixed salt, Since the fall of the melting point is also caused, the possibility of low-temperature composition is opened further greatly.

[0064]Reference example 9., next the reference example 9 are explained. 3.694 g, Ag_2O , and 11.587 g were mixed for Li_2CO_3 with the automatic mortar to Co_3O_4 and 8.023 g for 2 hours (Ag addition % of 10 mol). This powder mixture was calcinated at 850 ** among the air with the electric furnace for 20 hours. Since it decomposes in the middle of calcination and metal powder is generated, it is dramatically detailed and LiCoO_2 which metal powder distributed uniformly is obtained. Since a part of Ag replaces by Li when Ag_2O is used, as a constituent, it becomes $\text{Li}_{1-x}\text{Ag}_x\text{CoO}_2\text{:Ag}_y$ ($x+y=\text{addition}$). Since electrical conductivity of metal powder is high, a constituent with high electrical conductivity is obtained as a result. It was set to 52Kohm when the electric resistance value was measured.

[0065]making Ag_2O drawing 15 at Ag -- 10 and 20 or 30-mol% -- the TG-DTA measurement result (inside of the air) of the added sample ($\text{Co}_3\text{O}_4\text{:Li}_2\text{CO}_3$) was shown. Although the endothermic peak P1 from near 250 ** becomes so large that the addition of Ag increases, as for this, Ag_2O is a ***** thing at the reaction decomposed into Ag and O_2 , and weight loss is accepted in this temperature region (data accrued). Therefore, it is clear that the synthetic reaction of LiCoO_2 is advancing under coexistence of metal Ag in the temperature region beyond this temperature. Although the endothermic peak P2 from near 400 ** does not change with Ag additions so a lot, the elevated-temperature side endothermic peak from 850 ** is in the tendency which becomes so large that the addition of Ag increases (data accrued).

[0066]The X diffraction peak between $2\theta = 70 - 10$ was shown in drawing 16. Fundamentally, there are two, the diffraction peak of LiCoO_2 and the diffraction peak of metallic silver (an asterisk shows). The relation between Ag addition and diffraction intensity is shown in drawing 17. It turns out that the diffraction intensity from metallic silver increases with Ag concentration, and the

diffraction intensity from LiCoO_2 decreases conversely.

[0067]Although silver oxide was added in the above-mentioned reference example, it decomposes in the temperature region to calcination temperature, and other metallic oxides which generate metal powder, i.e., gold oxide, platinum oxide, iridium oxide, oxidation metal NIUMU, or oxidation palladium also has the same effect.

[0068]Reference example 10., next the reference example 10 are explained. 3.694 g, Cu_2O , and 7.154 g were mixed for Li_2CO_3 with the automatic mortar to Co_3O_4 and 8.023 g for 2 hours (Cu addition % of 10 mol). This powder mixture was calcinated at 850 °C among the air with the electric furnace for 20 hours. It was set to 13Kohm when the electric resistance value was measured (before addition 1 M ohm).

[0069]As a result of distributing uniformly in the LiCoO_2 powder which the oxide semiconductor with high electrical conductivity generated, a constituent with high electrical conductivity is obtained. Since a part of added Cu replaces by Li when especially Cu_2O is used, a constituent like $\text{Li}_{1-x}\text{Cu}_x\text{CoO}_2:(\text{Cu}_2\text{O})_y$ ($x+y$ = addition) is obtained. The pyrolysis of the Cu_2O is not carried out at 900 °C. Since the electrical conductivity is a semiconductor of the type going up so that NiO, FeO, Cr_2O_3 , MoO_2 , etc. are fully calcinated in the air in addition to Cu_2O and oxidation progresses, Since electrical conductivity improves further by oxidation at the time of the synthetic reaction of the constituent which uses LiCoO_2 or LiCoO_2 as the main ingredients, it is desirable.

[0070]NiO, FeO, and Cr_2O_3 have a possibility of replacing by Co rather than replacing by Li at the time of a LiCoO_2 synthetic reaction. That is, if NiO is added, for example, a constituent called $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2:\text{NiO}_y$ ($x+y$ = addition) will be obtained. The same may be said of addition of FeO and Cr_2O_3 .

[0071]The TG-DTA measurement result (inside of the air) of Cu addition sample (Cu=10, 20 or 30-mol%) was shown in drawing 18. Although the 370 to 470 °C endothermic peak P1 does not change with Cu concentration, the not less than 480 °C endothermic peak P2 and the endothermic peak P3 (a figure is an enlarged drawing) from 810 °C have it in the tendency which increases along with the increase in Cu concentration. The X diffraction result was shown in drawing 19. Its LiCoO_2 is fundamentally main although an asterisk shows the diffraction peak of Cu_2O . Although the diffraction peak of Co_3O_4 was seen to 30-mol% Cu addition% of 10 mol, since firing time was a sample for 30 minutes, this was not observed by the sample calcinated further for a long time.

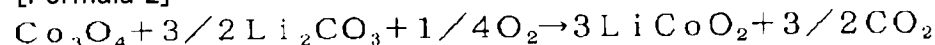
[0072]The diffraction intensity of three diffraction peaks (2 theta = 45.2 degrees, 37.3 degrees, 18.8 degrees) of Cu addition sample and Ag addition sample was respectively shown in drawing 20 (a) and (b). Since the density range where linearity is materialized is wide, Cu addition sample can guess that the density range which the Cu can replace by Li rather than Ag is wide.

[0073]Reference example 11., next the reference example 11 are explained. 3.694 g was mixed for MnO_2 , 8.181 g, and Li_2CO_3 with the automatic mortar to Co_3O_4 and 8.023 g for 2 hours (Mn addition % of 30 mol). This powder mixture was calcinated at 850 °C among the air with the electric furnace for 20 hours.

[0074]The synthetic reaction of LiCoO_2 is a reaction which needs excessive oxygen as shown in the following chemical formula.

[0075]

[Formula 2]



[0076]Usually, LiCoO_2 which carried out pyrogenic synthesis is holding hypoxia to the extent that it

becomes a problem. namely, LiCoO_{2-y} ($0 < y < 0.3$) -- the presentation -- oh, touch -- **. The oxygen generated from the oxide disassembled during LiCoO_2 composition compensates the above-mentioned amount of insufficient oxygen, and has an effect which improves stoichiometry.

[0077]In order to lessen an oxygen deficiency, there is also a synthetic method using the hyperoxidation oxide of lithium (M, G, S, R, Thomaset al., Mat.Res.Bull., 20(1985)1137).

[0078]A sample which replaced Mn by Co is explained. Additions of Mn are 10 and 20 or 30-mol%, and what were used is Co_3O_4 , MnO_2 , and Li_2CO_3 . A TG-DTA measurement result at the time of MnO_2 addition was shown in drawing 21. Irrespective of Mn addition, one endothermic peak is shown from near 360 ** to near 480 **. Since there is no thermal change in addition to this, Mn is considered that lithiation advances to the same extent as Co.

[0079]An X diffraction result measured between angle-of-diffraction $2\theta=70 - 10$ was shown in drawing 22. Quantity of a lithium manganic acid ghost is increasing as an addition of Mn increases.

An infrared absorption spectrum of MnO_2 addition was shown in drawing 23. A peak of wave number $^{-1}$ of 660 cm shown by an arrow is a peak peculiar to Spinel structure. Therefore, in a sample which added Mn from this infrared absorption spectrum, the layer structure of LiCoO_2 and Spinel structure of a lithiation manganic acid ghost live together, and it can be said that a crystal structure has composite-ized. A lithiation manganic acid ghost with Spinel structure is a leading candidate material which is equal to LiCoO_2 as a positive electrode material for highly efficient lithium secondary batteries. Since Spinel structure has many tunnel structures which can accommodate Li, Mn addition constituent with this composite-ized crystal structure has the outstanding lithium seating capacity. That is, a rechargeable battery with high capacity is obtained.

[0080]Na, K, Ag, Cu_2O , and MnO_2 which have so far been explained in Table 4 -- 5, 10, and 20 or 30-mol% -- an electric-resistance-measurement result of an added sample was shown.

[0081]

[Table 4]

試料 mol% 添加元素	LiCoO_2 (0mol%)	5(mol%)	10(mol%)	20(mol%)	30(mol%)
K	$1.0 \times 10^6 \Omega$	1.0×10^4	3.25×10^2	43	38
Na	1.0×10^6	1.4×10^5	2.0×10^4	1.7×10^4	3.1×10^3
Cu	1.0×10^6	1.0×10^5	1.3×10^4	5.0×10^3	4.0×10^3
Ag	1.0×10^6	2.0×10^5	5.2×10^4	3.1×10^3	41
Mn	1.0×10^6	2.0×10^6	4.2×10^6	4.4×10^6	4.5×10^6
N+Na	1.0×10^6	3.0×10^4	2.0×10^3	100	80

[0082]Electric resistance measurement of calcination powder was performed in the following procedure. 1g of calcination powder finely ground with a mortar of agate was taken, and it fabricated by a pressure of 2 ton/cm^2 in a 13-mm disk with a press. Both sides of this molding body were put with a copper plate, and electrical resistance was measured by a digital voltmeter.

[0083]A result of Table 4 is first compared with the above-mentioned literature value of LiCoO_2 .

Although it is an electric resistance value of LiCoO_2 , it will be set to 26.5 ohms if literature value cm of 100ohms raised previously is converted into this measurement circle board size. Our value is 1 M omega in Table 4. The cause of this inconsistency can consider particle diameter of a granular material, a difference in pressing pressure, etc. Since these concrete figures are not raised,

consideration beyond this is impossible.

[0084]K addition -- more than 20mol% -- 1/100,000 -- in Ag addition, it drops to 1/100,000 at more than 30mol%. In Cu addition, it drops to 1/1000 at more than 20mol%, and has dropped to 1/1000 in Na addition at more than 30mol%. The fall of electrical resistance is not seen in Mn addition.

[0085]Thus, by addition of K, Ag, Cu, and Na, LiCoO_2 with a high electric resistance value can be intrinsically made into low resistance, and the internal resistance of an anode can be decreased. In particular, it is remarkable with K additive and Ag additive. A remarkable effect is expectable also with Cu additive or Na additive.

[0086]Reference example 12., next the reference example 12 are explained. The evaluation from an infrared absorption spectrum (from 1000 to 200cm^{-1}) is described first. As mentioned above, a Co-O_6 elastic absorption band (600 cm) is divided into a normal part (A) and an un-normal part (B), and the computed surface ratio (B/A) is a parameter relevant to stoichiometry (O/Co). Hypoxia also becomes large, so that there is so little hypoxia in LiCoO_2 that a B/A ratio is small and a B/A ratio is large. As shown in drawing 24, in the relation between this B/A and the diffusion coefficient of the lithium ion in positive active material, a B/A value has the maximum near 2. The diffusion coefficient of the lithium ion was measured by the cyclic voltammetry method which is a general electrochemical measuring method. When the diffusion coefficient of a lithium ion has a large diffusion coefficient with regards to the current at the time of a cell reaction, its kinetic current is also large. A diffusion coefficient is used, and the value more than 10^{-12} is desirable, therefore, as for the range of B/A, 0.5 to 3.0 is desirable.

[0087]The extinction quotient of the absorption band (deformation vibration of Co-O_6 combination) of 247-cm^{-1} and the absorption band of 600-cm^{-1} is considered that the completeness of Co-O_6 combination is shown as mentioned above. Completeness is so low that this value is small, and it is so highly complete that this value is large. As shown in drawing 25, in the ratio of the absorbance of the absorption band of 247-cm^{-1} and the absorption band of 600-cm^{-1} which are considered to be an index which shows the completeness of Co-O_6 combination, the service capacity per active material weight increases to 4. Since service capacity suitable for practical use is considered to be 70 or more mAh/g, as a ratio of an absorbance, 0.5-4.0 are desirable.

[0088]As mentioned above, this evaluation of two points is a very important thing which can never be obtained from an X diffraction result. The conclusion from infrared absorption was shown in Table 5 about the additive.

[0089]

[Table 5]

添加元素	B/A比	(10mol%~30mol%) Co-O_6 結合の完成度
Na	0.72~0.84 (低い)	0.47~2.18 (10mol%) (30mol%)
K	1.4 で変わらない	0.5~1.8
Ag	1.56~1.78	0.41~0.48
Cu	1.1~1.4	0.39~0.46
Mn	0.93~1.12 (低い)	0.39~0.43

[0090]It is clear to have the effect that only Na and Mn make a B/A ratio small, in an alloying element. That is, addition of Na and Mn makes hypoxia hard to produce. Against it, K, Ag, and Cu do not have such a special effect, but give the completely same B/A ratio as an additive-free case.

[0091]Next, if it sees about the influence of the alloying element given to the completeness of the Co-O₆ combination also concerning the completeness of a crystal structure, Na and K will have the mostly alike effect and will receive the impression in which the direction of Na is a little excellent. It seems that it does not differ so much and does not have the specially outstanding effect about Ag, Cu, and Mn as compared with Na or K.

[0092]Reference example 13., next the reference example 13 are explained. This reference example describes a rechargeable battery which used the above positive electrode materials, and a manufacturing method for the same. Drawing 26 is a section lineblock diagram of the lithium secondary battery by this reference example, and used wet process as a molding method of an electrode layer. As a solvent, the anode dissolved PVdF3 weight section in NMP solution 33 weight section as a binder, used it as the binder solution, it made this solution distribute graphite powder 6 weight section as LiCoO₂ powder 58 weight section and a conducting agent as the positive active material 1, and created coating liquid. The long electrode sheet with a 30-cm thickness [in width] of about 150 micrometers was created after coating desiccation on the aluminum foil 4 with a thickness of 20 micrometers which is a charge collector about this coating liquid. The anode independent film sheet was created by removing from a coating substrate after coating desiccation so that it might be set to 30 cm in width, and about 150 micrometers in thickness on the coating substrate by which silicone coating was carried out still more nearly similarly.

[0093]As a solvent, the negative electrode dissolved PVdF3 weight section in NMP solution 33 weight section as a binder, used it as the binder solution, it made this solution distribute mesophase-microbeads carbon powder 62 weight section and the amount part of lithium carbonate duplexes as the negative electrode active material 2, and created coating liquid. The electrode sheet (31 cm in width and about 150 micrometers in thickness) was created after coating desiccation on the copper foil 5 with a thickness of 20 micrometers which is a charge collector about this coating liquid. The negative-electrode independent film sheet was created by removing from a coating substrate after coating desiccation so that it might be set to 31 cm in width, and about 150 micrometers in thickness on the coating substrate by which silicone coating was carried out still more nearly similarly.

[0094]As shown in drawing 26, the two-layer anode and negative electrode body which piled up the electrode independent film sheet were made to counter on the current-collecting-foil unification electrode body created to the separator 3, and the battery element structure folded up every 30 cm in the length direction at the 4 time ** face crease was created. The separator 3 is folded with the start of a chip box, and it was made to protrude every about 2 cm into the last each from an anode and a negative electrode. Then, such battery element structures were pressed by one, and contact of each member was raised.

[0095]The battery element of the created about 30-cm angle was inserted in the frame made from polyethylene, and it connected with the separator and reservoir which were protruded from the battery element, and inserted with two 0.1-mm-thick stainless plates further, and thermal melting arrival was carried out, pressing the circumference, and the square plate-like cell was created.

[0096]After putting the whole cell into the vacuum housing and making it a vacuum (less than - 750mmHg), the electrolysis solution which melted lithium perchlorate 1 mol/l in 1:1 mixed solvents of ethylene carbonate and dimethoxyethane was slushed into the pouring-in mouth provided beforehand. It performed pouring in in the dry box of dry carbon dioxide atmosphere, and the pouring-in mouth was welded and obturated after the completion of pouring in.

[0097]Thus, the assembled cell obtained the output of the cell voltage 3.6V and 162W, after charging to the first time cell voltage 4.2V. Since adhesion shaping was carried out and an electrode active material layer monolayer became thin after it carries out the electrode active material layer of a fold-up cell to more than two-layer and bending folds this up in this reference example, it became possible to perform a battery assembly, without the pliability which receives bending producing a

crack in increase and an electrode layer. When an electrode process was a wet compaction, since thickness became thin, even if it considered that shaping number of sheets increased, drying time was shortened and led to reduction of manufacture energies.

[0098]Reference example 14., next the reference example 14 are explained. In this reference example, anode coating liquid was created like the reference example 13. Coating of this coating liquid was carried out on aluminum foil with a thickness of 20 micrometers which is a charge collector, and the long electrode sheet with a 30-cm thickness [in width] of about 300 micrometers was created after desiccation. Negative-electrode coating liquid was created like the reference example 13. Several long electrode sheets with a 31-cm thickness [in width] of about 300 micrometers were created by carrying out coating of this coating liquid, and drying it on copper foil with a thickness of 20 micrometers which is a charge collector.

[0099]While going the slit 8 into the active material layers 1 and 2 of the portion which is equivalent to the bending part of the curvature 0 within a fold-up cell to be shown in drawing 27 as battery assembly preparation processing of the created anode and a negative electrode body, the active materials 1 and 2 equivalent to the bending part 9 with curvature were removed from the current collecting foil 4 and 5, and the electrode body was created. This anode and negative electrode are piled up so that an active material layer may face each other on both sides of the porous polypropylene film (50 micrometers in thickness) which is the separator beforehand cut by the required dimension, The battery element structure folded up 4 times was created inserting semicircular pillar-like porous body polypropylene material in the length direction as shown in drawing 28 as the spacer 6 every 30 cm at a clinch part.

[0100]The following battery assemblies were performed like the reference example 13, and did the cell examination. Thus, the assembled cell obtained the output of the cell voltage 3.5V and 158W, after charging to the first time cell voltage 4.2V. Even if it performed the long-term charging and discharging cycle, the remarkable fall of the characteristic was not seen. Thus, in this reference example, since the electrode active material layer of the curvature portion was removed, and an electrode layer is treated as a monotonous chisel and it is not necessary to bend it, a battery assembly is possible for it, without producing a crack. Since materials, such as an active material, can also be used without futility, the material yield of an electrode active material also improves. The portion which had the electrode of a curvature portion removed, The stable charging and discharging cycle can be expected without fracturing, in order to ease the stress which bends even if expansion and contraction of an electrode arise at the time of the function as an electrolyte reservoir being also not only expectable but cell charge and discharge, and requires the spacer of a portion for current collecting foil, since the semicircular pillar-like spacer is inserted.

[0101]Reference example 15., next the reference example 15 are explained. In this reference example, the long electrode of the continuation active material layer about 300 micrometers thick was created several sheets like the reference example 13. Then, as shown in drawing 29, three cells (electrode pair) were accumulated in parallel, and it folded up like the reference example 13, and finished setting up a cell, and the cell examination was done. It wired so that the lead 7 might be picked out from inner battery current collecting foil and the cell of three layers might serve as a parallel circuit. The cell assembled like the reference example 13 after this obtained the output of the cell voltage 3.7V and 500W, after charging to the first time cell voltage 4.2V. Even if it performed the long-term charging and discharging cycle, the remarkable fall of the characteristic was not seen.

[0102]Thus, in this reference example, since two or more cells were folded up in piles in parallel and the curvature of the electrode of a fold-up lateral part becomes larger than that of an inner part, the probability which produces a crack at the time of a battery assembly decreases. Since it is supported by the outside member, and intensity improves, generating of a crack is avoided [although the electrode of an inner part serves as small curvature]. Since the stress to the current collecting foil by swelling and contraction of an electrode layer furthermore becomes comparatively

small in a portion with large curvature also at the time of cell charge and discharge, the fracture of current collecting foil is controlled.

[0103]Reference example 16., next the reference example 16 are explained. In this reference example, the long electrode of the continuation active material layer about 300 micrometers thick was created several sheets like the reference example 15. Then, a fold-up battery element structure was assembled, piling up by turns the cell layer which intersects perpendicularly as shown in drawing 30 (a) and (b). The semicircular pillar-like spacer 6 was inserted in the bending part inside. It finished setting up a cell like the reference example 13 after that, and the cell examination was done. Thus, the assembled cell obtained the output of the cell voltage 3.7V and 666W, after charging to the first time cell voltage 4.2V. Even if it performed the long-term charging and discharging cycle, the remarkable fall of the characteristic was not seen. Thus, since it folded up overlapping two or more cells on each other in piles right-angled in this reference example and the curvature which folds up an electrode layer can be designed more greatly than electrode fracture curvature, it becomes easy to fold up an electrode layer, without producing a crack, and a manufacturing yield improves. Since the stress to the current collecting foil according to swelling and contraction of an electrode layer since curvature is large furthermore becomes comparatively small also at the time of cell charge and discharge, the fracture of current collecting foil is controlled.

[0104]Reference example 17., next the reference example 17 are explained. In this reference example, in accordance with the method of the reference example 13, coating of the electrode coating liquid was carried out on the after-creation silicone coating substrate, and the anode and negative-electrode independent film sheet was created so that it might be set to after-desiccation about 300 micrometers in thickness. Cut this on cell flat-surface area a square of 30 cm, the battery element was made to constitute so that it may become the composition of drawing 28, battery element structure was pressed by one like the reference example 13 below, and contact of each member was raised. Thus, the assembled cell obtained the output of the cell voltage 3.5V and 158W, after charging to the first time cell voltage 4.2V. Even if it performed the long-term charging and discharging cycle, the remarkable fall of the characteristic was not seen.

[0105]Comparative example 1 ... Electrode coating liquid was created like the reference example 13, coating desiccation was carried out on current collecting foil, and the electrode sheet of the anode with a comparatively high active material filling factor and the negative electrode was created by creating and pressing a 300-micrometer-thick monolayer coat sheet. Sheet size is the same as that of the reference example 13. The anode and negative electrode body which piled up the electrode independent film sheet were made to counter like the reference example 13 on the current-collecting-foil unification electrode body created to the separator, and the battery element structure folded up to the 4 time ** face crease every 30 cm was created in the length direction as shown in drawing 31. Although the crack might arise in the electrode layer in the bending portion or the electrode active material layer might separate from current collecting foil at the time of this process, battery element composition was created like the reference example 13. Then, except having excluded like the press operator of a battery construction element, the cell was assembled like the reference example 13 and the cell examination was done. Thus, the assembled cell obtained the output of the cell voltage 3.3V and 148W, after charging to the first time cell voltage 4.2V. When a long-term charging and discharging cycle was performed, the decreasing rate of the characteristic was comparatively large.

[0106]Comparative example 2 ... Electrode coating liquid was created like the comparative example 1, coating desiccation was carried out on current collecting foil, and the monolayer coat sheet about 300 micrometers thick was created. Battery element composition was created like the reference example 13 using the sheet which is not pressed [this], and after the battery assembly, as a result of doing a cell examination similarly, the output of the cell voltage 3.4V and 153W was obtained. When a long-term charging and discharging cycle was performed, the decreasing rate of the

characteristic was comparatively large.

[0107]As mentioned above, after folding up the electrode active material layer where the degree of stoma is comparatively high in the state of un-pressing, that a battery characteristic improves became whether to be ** by pressing.

[0108]Embodiment 1., next the embodiment of the invention 1 are described. In the lithium secondary battery using [using an inorganic oxide as positive active material at this embodiment] carbon as negative electrode active material, It aims at making a filling factor increase by mixing the granular material of particle diameter in which the mean particle diameter of the inorganic oxide which is positive active material, or the carbon which is negative electrode active material differs. That is, when the close-packed structure has cubic close packed structure and hexagonal close-packed structure and the particle is made into a globular form in the granular material of single mean particle diameter, in a model top, the filling factor is about 0.76. However, a filling factor can be made to increase further by mixing the particles of a diameter of a granule which is in the opening between this particle to the particles of this large diameter.

[0109]As a coating solvent, PVdF3 weight section was dissolved in NMP solution 33 weight section as a binder, and it was considered as the binder solution. In this solution, as positive active material, cobalt-acid-lithium powder is added so that it may become a large diameter granular material which is the mean particle diameter of 10 micrometers with the weight ratio 0.2 of the diameter of a granule to a large diameter about the diameter granular material of a granule which is the particle size ratio 0.05, and it was made to become 58 weight sections on the whole. This was made to distribute graphite powder 6 weight section as a conducting agent, and coating liquid was created. About 150-micrometer electrode sheet was created by carrying out coating of this coating liquid, and drying it on aluminum foil with a thickness of 20 micrometers which is a charge collector. The filling factor of the electrode was obtained by measuring the weight and volume of this electrode. As a result compared with the case of the active material granular material of the single mean particle diameter shown according to the comparative example 3, the filling factor increased the filling factor by about 20%.

[0110]Comparative example 3 ... Except having used only the active material which is the mean particle diameter of 10 micrometers, the electrode sheet was created like Embodiment 1 and same evaluation was performed. The filling factor was 0.61.

[0111]Thus, the filling factor of an active material can be raised by mixing at least two or more kinds of granular materials in which particle diameter differs in an anode and negative electrode active material. The service capacity per unit volume can be made to be able to increase by this, and battery capacity can be raised. By the above-mentioned embodiment, when a granule child's particle diameter set a large drop child's particle diameter to 1, the example of 0.05 was shown, but if the ratio of a granule child's particle diameter is 0.3 or less, it has the same effect.

[0112]Embodiment 2., next the embodiment of the invention 2 are described. According to this embodiment, by mixing at least two or more kinds of carbon in which the potential characteristics differ in negative-electrode carbon, negative-electrode potential is raised and it aims at suppressing a deposit of the lithium metal in a negative electrode. It turns out that carbon differs in the characteristic of a granular material greatly by a starting material, calcination temperature, and firing time. Therefore, also in the carbon used for a negative electrode, the electrode characteristic changes with kinds of carbon, and differences, such as capacity and potential, are great. Therefore, by mixing the carbon powder object in which these characteristics differ, the carbon electrodes in which the potential characteristics differ can be created.

[0113]As a coating solvent, PVdF5 weight section was dissolved in NMP solution 45 weight section as a binder, and it was considered as the binder solution. this solution -- electrode potential with carbon powder independent as negative electrode active material -- about -- about [what is 0V, and] -- added what is 0.2V so that it might become the weight ratio 1 to 1, and it is made to become 50 weight sections on the whole, and coating liquid was created. About 100-micrometer

electrode sheet was created by carrying out coating of this coating liquid, and drying it on copper foil with a thickness of 20 micrometers which is a charge collector. The filling factor of the electrode was obtained by measuring the weight and volume of this electrode. In the coin type cell, cobalt acid lithium was used for the anode, the mixed liquor of ethylene carbonate / dimethoxyethane / lithium perchlorate was used for the electrolysis solution, and the cell examination was done. As a result, rather than the independent case, descent of average potential could be controlled and the deposit of a lithium metal was able to be controlled.

[0114]Comparative example 4 ... Except saying that average electrode potential used only the carbon which is about 0V, when the electrode sheet was created like Embodiment 2 and same evaluation was performed, average electrode potential became less than 0V, and the deposit of the lithium metal after cell decomposition was found.

[0115]Embodiment 3., next the embodiment of the invention 3 are described. According to this embodiment, it is related with the improvement in service capacity by rationalization of an anode presentation. Since the two electrodes of the lithium secondary battery use the granular material, in order to fabricate, they need to add a binder. However, a superfluous quantity has a possibility of checking an electrode reaction. When there are many binder amounts as mentioned above, an active material filling factor may be influenced. For this reason, the result of having examined the appropriate value which took into consideration the moldability of a slurry, the flexibility of electrode structure, the active material filling factor, and the electrode reaction, When the binder was covered by the surface of the positive active material which is a granular material, and a conducting agent, average covering thickness t_B (nm) of the binder presupposed that the range of $3 \leq t_B \leq 16$ is an appropriate value of a binder.

[0116]The binder solution which dissolves PVdF in NMP solution 30 weight section as a coating solvent, and dissolves 1.5 to 4 weight sections as a binder and in which concentration differs was created. This solution was made to distribute graphite powder 6 weight section as cobalt-acid-lithium powder 60 weight section and a conducting agent as positive active material, and coating liquid was created. About 150-micrometer electrode sheet was created by carrying out coating of this coating liquid, and drying it on aluminum foil with a thickness of 20 micrometers which is a charge collector. About these electrodes, in the coin type cell, carbon electrodes were used for the negative electrode, the mixed liquor of ethylene carbonate / dimethoxyethane / lithium perchlorate was used for the electrolysis solution, and the cell examination was done. The result is shown in drawing 32. When the presentation of the binder increased as a result and the covering thickness in the powder surface exceeded 16 (nm), it turned out that service capacity decreases rapidly. As for intensity and a moldability to covering thickness, more than 3 (nm) is desirable.

[0117]Embodiment 4., next the embodiment of the invention 4 are described. According to this embodiment, it is related with the improvement in a filling factor by rationalization of an anode presentation. Since positive active material is an inorganic oxide and lacking in electronic conductivity, black lead is thrown in as a conducting agent. If the black lead concentration in an electrode increases, electronic resistance of an electrode will decrease, but the filling factor of an active material will decrease. For this reason, the appropriate value was examined in the filling factor and electrode resistance of an active material, and the appropriate value of black lead concentration was calculated. This density range is explained in drawing 33. Active material filling factor ϕ_A and black lead filling factor ϕ_G are shown on volume fraction x_A (as for $=V_A/(V_A+V_G)$ and V_A , active material volume and V_G are graphite body products) of an active material, and a vertical axis by the horizontal axis of this figure. It turns out that an active material filling factor goes up, so that an active material volume fraction rises from this figure. However, it turns out that a filling factor is saturated in a certain concentration. If the value of this closest packing is made into ϕ_{AC} and the active material volume fraction at this time is made into x_{AC} , the black lead concentration at this

time will serve as $1-x_{AC}$. Therefore, if it is below this concentration, an active material filling factor will become the closest packing. However, since resistance became large when black lead concentration became low, as a minimum community of concentration, it determined from the quantity of the voltage loss by resistance rise. That is, the range of the following $[x_G / (V_G / (V_A + V_G))] / \text{graphite body integration rate } x]$ is the optimal.

$(1-x_{AC}) / 3 \leq x_G \leq 1-x_{AC}$ [0118] As a coating solvent, as a binder, in NMP solution 30 weight section, binder covering thickness was dissolved so that it might be set to 12 nm, and PVdF was used as the binder solution at it. This solution was made to distribute eight weight sections from the graphite powder 3 as cobalt-acid-lithium powder 60 weight section and a conducting agent as positive active material, and coating liquid was created. About 150-micrometer electrode sheet was created by carrying out coating of this coating liquid, and drying it on aluminum foil with a thickness of 20 micrometers which is a charge collector. The filling factor of the electrode was obtained by measuring the weight and volume of this electrode. Electronic resistance of this electrode was measured in MIRIO meter. In the coin type cell, carbon electrodes were used for the negative electrode, the mixed liquor of ethylene carbonate / dimethoxyethane / lithium perchlorate was used for the electrolysis solution, and the cell examination was done. The result is shown in drawing 35 from drawing 34. As a result, when black lead concentration is lowered, it turns out that an active material filling factor is saturated with a certain black lead concentration, and if below this concentration creates an electrode by $x_G \leq 0.13$, it turns out that an active material filling factor becomes the highest value (drawing 34). However, since black lead is a conducting agent, when composition ratio falls, it turns out that electronic resistance of an electrode increases (drawing 35). Therefore, it is good to consider it as $0.05 \leq x_G$.

[0119] Embodiment 5., next the embodiment of the invention 5 are described. According to this embodiment, it is related with improvement in the service capacity by rationalization of an electrode presentation. It is porosity, an electrolysis solution enters in the meantime, and the electrode is performing the active material and the reaction. Therefore, it is necessary for the opening which this electrolysis solution enters to recognize adequate amount existence. The appropriate value of voidage P (%) has the good range of $10 \leq P \leq 30$.

[0120] That is, the voidage of the anode created by Embodiment 4 from Embodiment 1 was measured, and the relation between this value and the service capacity per weight was shown in drawing 36. When voidage became 10% or less as a result, it turned out that service capacity decreases rapidly. When it became not less than 30%, it turned out that the service capacity per volume falls.

[0121] The figure showing the rate of the increase in the service capacity at the time of making a filling factor increase by improvement of electrode structure is shown in drawing 37. It turns out that service capacity increases, so that a filling factor is made to increase from this figure.

[0122] As for the rate over binder 1 weight section of the coating solvent in electrode creation, in the electrode of the lithium secondary battery shown in Embodiment 5 from Embodiment 1 above, it is preferably desirable that it is eight to 20 weight section five to 30 weight section. As an example of a manufacturing method, this binder is dissolved in a coating solvent, a binder solution is created, and there are the method of fabricating the thing which made this solution distribute an active material etc. on a base or an electrode collector, etc. Although limitation in particular is not carried out as the above-mentioned binder, especially a fluoro-resin is preferred and polyvinylidene fluoride (PVdF), polytetrafluoroethylene (PTFE), etc. are mentioned as an example. If said binder may be dissolved as the above-mentioned solvent, limitation in particular will not be carried out, but as an example, N-methyl pyrrolidone (NMP), N, N dimethylformamide (DMF), etc. are mentioned. Although limitation in particular is not carried out as the above-mentioned negative electrode active material, as an example, carbon materials, such as graphite, glassy carbon, carbon black, corks, pyrolytic

carbon, and carbon fiber, are mentioned. Although limitation in particular is not carried out as the above-mentioned positive active material, As an example, inorganic compounds, such as TiS_2 , MoS_2 , MnO_2 , and V_2O_5 , V_6O_{13} , LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , etc. are enumerated. As the above-mentioned charge collector, foil, such as copper, aluminum, nickel, iron, and stainless steel, a mesh, an expanded metal, etc. are mentioned. When using for a nonaqueous electrolyte battery the electrode created as mentioned above using this binder, it can use also as a negative electrode or an anode, and there is in particular nothing that is limited also for the electrolyte or electrolysis solution of this cell, and the same thing as usual can be used.

[0123]

[Effect of the Invention]As mentioned above, in the lithium secondary battery using [using an inorganic oxide as positive active material] carbon as negative electrode active material according to this invention, The mean particle diameter of the carbon which is the inorganic oxide or negative electrode active material which is positive active material comprises at least two or more kinds, When the ratio of the particle diameter of a granule child when referred to as 1 makes the particle diameter of the 1st particle the lithium secondary battery electrode structure which is 0.3 or less, rather than before, the high electrode of an active material filling factor can be obtained, the service capacity per unit volume can be raised, and the performance of a lithium secondary battery can be raised.

[0124]By making it the lithium secondary battery electrode structure which the raw material, the manufacturing conditions, or the characteristic of carbon which is negative electrode active material is different, and comprises at least two or more kinds in the lithium secondary battery with which negative electrode active material comprises carbon, The potential drop of the negative electrode was able to be controlled. For this reason, the deposit of the lithium metal due to the fall of the potential within negative-electrode carbon could be prevented, and a cycle life's life was able to be prolonged by controlling the capacity lowering and the electrode internal short circuit by metal-izing of a lithium ion.

[0125]In the lithium secondary battery with which an anode presentation comprises the inorganic oxide which is positive active material, black lead which is conducting agents, and the binder which is forming assistants, When the binder which is a forming assistant has covered on the surface of the positive active material which is a granular material, and a conducting agent, When average covering thickness t_B (nm) of a binder created the lithium secondary battery electrode structure which is the range of $3 \leq t_B \leq 16$, inhibition of the reaction of the lithium ion in an active material surface with a binder could be prevented, and the service capacity per weight was able to be raised.

[0126]In the lithium secondary battery with which an anode presentation comprises the inorganic oxide which is positive active material, black lead which is conducting agents, and the binder which is forming assistants, When an active material makes x_{AC} the active material volume fraction used as the closest packing, the high electrode of an active material filling factor can be created by making it the lithium secondary battery electrode structure which has graphite body integration rate x_G in the following ranges.

The electrode with large service capacity per unit volume could be created for $(1-x_{AC}) / 3 \leq x_G \leq 1-x_{AC}$ **, and, moreover, resistance of the electrode was also able to be made into the proper value.

[0127]In the lithium secondary battery which uses carbon as negative electrode active material using an inorganic oxide as positive active material, The reaction of the lithium ion between an active material and an electrolysis solution was able to become smooth, and the service capacity per weight was able to be made to increase by making it the lithium secondary battery electrode

structure which has the voidage P (%) in an electrode within the limits of $10 \leq P \leq 30$.

[Translation done.]